



# **Composition and bioavailability of DOC across a rural-urban gradient**

**Todd Andrew Wallace**

Environmental Biology  
School of Earth and Environmental Sciences  
The University of Adelaide  
Cooperative Research Centre for Water Quality and Treatment

A thesis submitted for the degree of  
Doctor of Philosophy

April 2006

# Contents

<b>Contents .....</b>	<b>i</b>
<b>List of Figures .....</b>	<b>viii</b>
<b>List of Tables .....</b>	<b>xvi</b>
<b>Declaration.....</b>	<b>xviii</b>
<b>Acknowledgments.....</b>	<b>xix</b>
<b>Summary.....</b>	<b>xx</b>
<b>Chapter 1: General Introduction.....</b>	<b>1</b>
1.1 Introduction .....	1
1.2 The Project .....	6
1.2.1 The relationship between particle size and biochemical oxygen demand .....	8
1.2.2 Impact of urbanisation on organic carbon composition and bioavailability .....	9
1.2.3 Effect of replacing native vegetation with introduced species on NOM processes .....	10
1.2.4 Internal and external loading of critical pollutants.....	11
1.2.5 The impact of urbanisation on the ability of stream reaches to intercept organic carbon.	12
1.3 Summary .....	12
<b>Chapter 2. General Methods.....</b>	<b>14</b>
2.1 Catchment Description.....	14
2.2 Locations of sampling sites .....	16
2.3 Sample Containers.....	16

2.4 Preparation of GF/C filters .....	16
2.5 Five-day Biochemical Oxygen Demand .....	16
2.6 Dissolved Oxygen .....	17
2.7 Dissolved Organic Carbon .....	17
2.8 Time series assessment of BOD and DOC biodegradability .....	18
2.9 Ion-exchange fractionation.....	21
2.9.1 Resin Cleaning Procedure .....	21
2.9.2 Loading Resin Columns .....	22

### **Chapter 3: Relative importance of particulate and dissolved organic carbon across the rural-urban gradient of the Torrens Catchment ..... 26**

3.1. Introduction .....	26
3.2. Materials and methods .....	27
3.2.1 Catchment Description .....	27
3.2.2 Relationship between TOC, POC and DOC .....	28
3.2.3 Relationship Between TSS and B.O.D. <sub>5</sub> .....	29
3.2.4 Relationship between total B.O.D. <sub>5</sub> and filtered B.O.D. <sub>5</sub> .....	30
3.2.5 Particle size distribution of oxygen demanding substances .....	30
3.2.6 Data Analysis .....	30
3.3. Results .....	31
3.3.1 Relationship between TOC and DOC .....	31
3.3.2 Relationship Between TSS and B.O.D. <sub>5</sub> .....	31
3.3.3 Relationship between total B.O.D. <sub>5</sub> and filtered B.O.D. <sub>5</sub> .....	31
3.3.4 Particle size distribution of oxygen demanding substances .....	32
3.4. Discussion .....	34

**Chapter 4: Characterisation of the composition and bioavailability of dissolved organic carbon across the rural-urban gradient in the Torrens Catchment. .... 39**

4.1 Introduction. .... 39

4.2 Methodology ..... 40

    4.2.1 Catchment Description and Sampling Sites ..... 40

    4.2.2 Sample Collection ..... 41

    4.2.3 Biochemical Oxygen Demand – Dissolved Organic Carbon ratios: Baseline Data ..... 41

    4.2.4 Carbonaceous biochemical oxygen demand, SUVA, and DOC depletion. .... 41

    4.2.5 Characterisation of DOC – relationship to bioavailability ..... 42

4.3 General methods..... 43

    4.3.1 Sample preparation..... 43

    4.3.2 Carbonaceous Biochemical Oxygen Demand..... 44

    4.3.3 Bioassays – supplementary nutrients ..... 44

    4.3.4 Dissolved Oxygen ..... 44

    4.3.5 Dissolved Organic Carbon ..... 45

    4.3.6 Specific Ultra Violet Absorbance (SUVA<sub>254</sub>)..... 45

    4.3.7 Data Analysis ..... 45

4.4 Results ..... 46

    4.4.1 Biochemical Oxygen Demand – Dissolved Organic Carbon ratios: Baseline Data ..... 46

    4.4.2 Carbonaceous biochemical oxygen demand, SUVA, and DOC depletion ..... 46

    4.4.3 Carbonaceous oxygen demand and ion exchange fractionation of DOC..... 49

4.5. Discussion ..... 54

    4.5.1 Biochemical Oxygen Demand – Dissolved Organic Carbon ratios: Baseline Data ..... 54

    4.5.2 Carbonaceous biochemical oxygen demand, SUVA, and DOC depletion ..... 54

    4.5.3 Relationship between BOD, bDOC and DOC composition: Tributary streams ..... 56

    4.5.4 General Discussion..... 57

## **Chapter 5: Characterisation of dissolved organic carbon bioavailability in an urban weir pool..... 59**

5.1. Introduction .....	59
5.2. Methodology .....	60
5.2.1 Site Description .....	60
5.2.2 Sample Collection .....	61
5.2.3 Carbonaceous Biochemical Oxygen Demand & Dissolved Organic Carbon Metabolism – Laboratory Study.....	61
5.2.4 In-situ study of dissolved oxygen and DOC concentrations .....	62
5.2.5 Dissolved Organic Carbon .....	63
5.2.6 Data Analysis .....	63
5.3. Results .....	63
5.3.1 Carbonaceous Biochemical Oxygen Demand & DOC depletion – Laboratory Study .....	63
5.3.2 In-situ study of dissolved oxygen and DOC concentrations .....	64
5.4. Discussion .....	70
5.4.1 Integrated discussion on laboratory and in-situ studies of DOC dynamics .....	70
5.4.2. General Discussion.....	73

## **Chapter 6: Relative composition and bioavailability of nutrients leached from leaf litter and garden waste..... 78**

6.1 Introduction .....	78
6.2 Materials and Methods .....	80
6.2.1 Leaf litter (plant material) collection .....	80
6.2.2 Preparation of leachate- FRP and DOC release .....	80
6.2.3 Oxygen demand and biodegradability of DOC released from plant material.....	81
6.2.4 Fractionation of the DOC pool.....	82
6.2.5 Analytical methods.....	82
6.2.6 Data Analysis .....	83

6.3 Results .....	83
6.3.1 FRP release.....	83
6.3.2 DOC release .....	83
6.3.3 Oxygen demand and biodegradability of DOC released from plant material.....	85
6.3.4 Fractionation of the DOC pool.....	87
6.4 Discussion .....	92
6.4.1 FRP and DOC release .....	92
6.4.2 Biochemical Oxygen Demand .....	93
6.4.3 DOC metabolism.....	94
6.4.4 Characterisation of DOC via ion-exchange fractionation.....	95
6.4.5 General Discussion.....	96

## **Chapter 7: A comparison of pelagic and sediment oxygen demand and phosphorus dynamics in an urban weir pool. .... 99**

7.1 Introduction .....	99
7.2 Methodology .....	101
7.2.1 Site Description .....	101
7.2.2 Sample Collection .....	101
7.2.3 Sediment Oxygen Demand.....	102
7.2.4 Sediment Composition .....	104
7.2.5 Benthic flux of filterable reactive phosphorus .....	105
7.2.6 Data Analysis .....	105
7.3 Results .....	106
7.3.1 Oxygen Demand Curves .....	106
7.3.2 Sediment Oxygen Demand.....	107
7.3.3 Benthic Demand Index.....	110
7.3.4 Sediment Composition .....	111
7.3.5 Benthic flux of filterable reactive phosphorus .....	112
7.4 Discussion .....	114

7.4.1 Sediment oxygen demand .....	114
7.4.2 FRP release.....	115
7.4.3 General Discussion.....	117

## **Chapter 8: The role of stream condition in DOC retention in an urbanised stream..... 118**

8.1 Introduction .....	118
8.2 Methodology .....	120
8.2.1 Site Description .....	120
8.2.2 Short-term DOC addition experiments .....	122
8.2.3 Calculation of in-stream parameters and Solute Transport Modelling .....	123
8.2.3.1 Stream Discharge .....	123
8.2.3.2 Dilution of the spike solution .....	124
8.2.3.3 In-stream retention time .....	124
8.2.3.4 Interception of DOC – percent uptake. ....	124
8.2.3.5 Solute Transport Modelling .....	124
8.2.4 Data Analysis .....	127
8.3 Results .....	127
8.3.1 Stream Discharge .....	127
8.3.2 Dilution of the spike solution.....	128
8.3.3 In-stream retention time .....	130
8.3.4 In-stream Velocity.....	131
8.3.5 Interception of DOC – percent uptake .....	132
8.3.6 Uptake length .....	134
8.3.7 Solute Transport Modelling: dispersion, retardation factor, decay and production coefficients .....	136
8.3.8 Assessment of the ability of the contrasting stream reaches to process the point source input.....	136
8.4. Discussion .....	139

8.4.1 Discharge.....	139
8.4.2. Dilution.....	140
8.4.3 Interception of DOC – Uptake Lengths and Percent Uptake .....	141
8.4.4 General Discussion.....	143

## **Chapter 9. General Discussion..... 145**

9.1 Introduction .....	145
9.2 Synthesis of findings .....	145
9.3 Implications for catchment management .....	148
9.4 Conclusions .....	151

## **Bibliography ..... 154**



## Summary

A great deal of attention has been focused on the effects of changes in land use on the physical and chemical conditions of streams and riparian zones. There is also currently substantial momentum and effort directed at restoring these areas. However, there is a distinct lack of understanding of not only the processes that occur in natural systems, but also the impact that changes in land use have actually had on those systems, and of how the “restored” system will function post intervention. The objective of this thesis was to examine the impact of urbanisation on the composition, and bioavailability and retention of organic carbon in streams.

Changes in composition, and bioavailability of organic carbon in stream water were investigated across rural-urban gradients in sub-catchments of the Torrens River, a mediterranean catchment in southern Australia. The influence of land use on the relative proportion of particulate and dissolved organic carbon, and the importance of different size fractions of the total organic carbon pool in driving biochemical oxygen demand (B.O.D.<sub>5</sub>) was assessed under base flow and storm flow conditions. Despite an expectation that an increased proportion of oxygen demanding material would be comprised of particulate material in the urbanised catchments, the results demonstrate that dissolved organic carbon comprises a substantial component of the organic carbon pool in both the rural (83%) and urban (89%) sites. Furthermore, although particulate material actually represents a higher proportion of oxygen demanding material in the rural sites (23%) than in the urban sites (4%), the difference is not statistically significant.

Bioassays performed on stream water samples demonstrated that DOC from the urbanised streams was more bioavailable than in the rural streams; the DOC in the urban streams exerted an oxygen demand per unit organic carbon 2.75 times higher than the rural streams. Furthermore, the DOC in samples from the urban streams was depleted in an exponential manner. In contrast, DOC was depleted in a slow, linear manner in samples from the rural streams. Ion-exchange fractionation of the samples revealed significant differences in urban and rural stream water DOC that demonstrates that urbanisation induces a substantial shift away from the naturally occurring range of DOC compounds (e.g. humic and fulvic acids, carbohydrates, oligosaccharides, polysaccharides) towards synthetic compounds (e.g. synthetic detergents, hydrocarbons, pesticides) which is correlated with an increase in BOD:DOC ratios. However, an assessment of the impact of inflowing stormwater on

DOC dynamics and water quality in Torrens Lake (a shallow urban weir pool) demonstrated that the DOC fractions most readily depleted and therefore most likely to be the most problematic, oxygen demanding organic compounds were the aquatic humic substances (e.g. humic and fulvic acids), and hydrophilic acids (e.g. fatty acids, sugar acids, hydroxyl acids).

The shift from native tree species to introduced deciduous species that commonly occurs in urbanised areas may have a series of profound effects on ecosystem function and stability. Bioassays and ion-exchange fractionation revealed that DOC released from the introduced species (English elm, London plane tree, white poplar and introduced grasses) has a distinctly different composition than that leached from a common native species (river red gum). Observed imbalances in DOC:FRP ratios and DOC metabolism kinetics between the different species indicates that changes in dominant vegetation may have serious implications on biogeochemical cycles. Furthermore, the rapid release of DOC from all litter types tested indicates that if gross pollutant traps (designed and installed to protect streams from pollutants such as leaf litter) are not cleared for 48-72 hours after the onset of rain, the majority of water soluble, oxygen demanding material will still enter the receiving water.

Sediment core studies revealed that although undisturbed and resuspended sediments generate a substantial oxygen debt ( $0.8$  and  $1.4 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  respectively), external loading of oxygen demanding organic material is responsible for the episodic deoxygenation of the water column that is often observed in Torrens Lake following rain events. Furthermore, although internal loading of filterable reactive phosphorus (FRP) from sediments ( $17 \text{ mg FRP m}^{-2} \text{ day}^{-1}$ ) represents a major source of bioavailable P that is potentially available to support algal blooms, external loading from inflowing stormwater ( $40 \mu\text{g FRP L}^{-1}$ ) continues to represent a major management concern and impediment to controlling the episodic nuisance and harmful algal blooms experienced in the Torrens Lake.

Urbanisation induced changes to the ability of a stream to retain DOC was assessed in three contrasting stream reaches; a reach that has retained a complex geophysical channel structure, a reach that has been converted to an open concrete channel, and a reach that has been converted to an underground concrete channel. DOC uptake kinetics in the degraded reach were characterised by long retention times, increased dilution, and comparatively short uptake lengths ( $79.9 \pm 7.4 \text{ m}$ ). In

comparison, the heavily engineered concrete channel was characterised by high water velocities and long uptake lengths ( $273.9 \pm 43.8\text{m}$ ). In contrast to the engineered reaches, the degraded reach maintained a relatively stable expected peak DOC concentration, uptake length and percent uptake, indicating that restoring stream complexity in urbanised streams by removal of concrete channels and reconstruction of natural meandering flow paths has a major role for improving the buffering capacity of urban streams.